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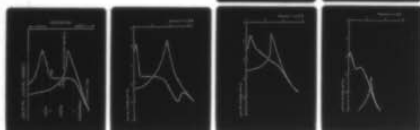
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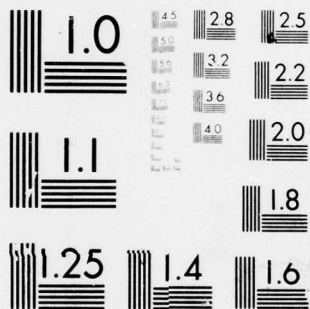
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ELECTROCHEMICAL BEHAVIOR OF GOLD ALLOYS

Eugene F. Huget  
Stanley G. Vermilyea  
Faris A. Modawar  
Laszlo B. de Simon

Division of Dental Materials  
U.S. Army Institute of Dental Research  
Washington, D.C. 20012

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Reactions resulting from polarization of five dental golds were studied. Test materials included an ADA certified type III alloy (Oro B-2) three "economy" alloys (Midas, Neycast and Minigold) and a high-fusing alloy (Olympia). The solvent was dilute lactated Ringer's solution ( $[Cl^-] \sim 24$ m Eq/L). Anodic scans over potentials of -0.1 to +1.9 V vs SCE defined the active, passive and trans-passive ranges of the alloys. Anodic polarization curves gave values for primary passive potential (Epp) and critical current density (Ic). Reduction phe-		

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nomena were observed with cathodic scans over potentials of +1.9 to -0.1 V vs SCE. Intersection of anodic and cathodic curves delineated corrosion potential ( $E_{corr}$ ) and corrosion current density ( $I_{corr}$ ). Potentials required to elicit a noble to active transition ranged from +.020 V for Neycast to +.093 V for Olympia. The range of primary passive potentials was marked by observations on Olympia ( $E_{pp}$  +.150 V) and Oro B-2 ( $E_{pp}$  +.200 V). At the onset of passivation Neycast and Olympia experienced the highest ( $I_c$   $4.93 \times 10^{-3}$  ma/cm<sup>2</sup>) and lowest ( $I_c$   $2.20 \times 10^{-4}$  ma/cm<sup>2</sup>) current densities, respectively. Respective  $E_{corr}$  and  $I_{corr}$  values were as follows: Oro B-2 +.527 V,  $4.13 \times 10^{-3}$  ma/cm<sup>2</sup>; Midas +.653 V,  $1.70 \times 10^{-2}$  ma/cm<sup>2</sup>; Neycast +.613 V,  $4.67 \times 10^{-2}$  ma/cm<sup>2</sup>; Minigold +.540 V,  $1.02 \times 10^{-2}$  ma/cm<sup>2</sup>; Olympia +.596 V,  $9.4 \times 10^{-4}$  ma/cm<sup>2</sup>. Analysis of electrochemical profiles revealed that at a chloride ion concentration comparable to that of human saliva ( $[Cl^-] \approx 24$  mEq/L), only Oro B-2 and Olympia exhibited the ability to passivate spontaneously.

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## ELECTROCHEMICAL BEHAVIOR OF GOLD ALLOYS

Historically, gold alloys have enjoyed extensive usage in the restoration of damaged and missing teeth. Preference for these materials over other available alloys has been predicated not only upon the mechanical and manipulative features of the dental golds but also upon their ability to resist destructive dissolution and tarnish.

For the most part, alloys meeting the compositional requirements of American Dental Association Specification No. 5 for dental casting gold alloy exhibit adequate resistance to in vivo tarnish and corrosion. In recent years, however, alloys containing less gold but more palladium, silver and base metal constituents than conventional crown and bridge alloys have become available for clinical use. Unfortunately, data that would either substantiate or refute the capability of many of these substances to resist corrosion are not available.

The present investigation was designed to allow comparative assessment of the corrosion behavior of five proprietary dental golds.

### Materials and Methods

Materials subjected to in vitro testing included an ADA certified type III alloy,\* three "economy" alloys<sup>+</sup> and a gold-palladium

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\* Oro B-2, The J. M. Ney Co., Hartford, CT 06101.

+ Midas (noble metal content 52.4%), J. F. Jelenko and Co., Pennwalt Corp., New Rochelle, NY 10801. Neycast (noble metal content 49.7%), The J. M. Ney Co., Hartford, CN 06101. Minigold (noble metal content 44%), Williams Gold Refining Co., Buffalo, NY 14214.



based high fusing alloy.<sup>#</sup> Cylindrical (4 mm X 6 mm) test pieces were cast from each material through the use of conventional lost wax dental laboratory procedures. Each metal cylinder was force-fitted into an immersible, nonconductive Teflon fixture (Figure 1). The exposed planar test surface of each specimen was polished manually on 600-grit metallurgical paper, cleansed in detergent, rinsed with alcohol and air dried. Then the specimen-fixture couple was threaded to a metal rod (potentiostat-specimen connector) and lowered into a glass corrosion cell.

Cyclic polarization of the alloys was accomplished in a solvent consisting of 1 part by volume lactated Ringer's solution<sup>§</sup> (chloride ion concentration 109 m Eq per L) and 4.5 parts by volume deionized water. Temperature of the medium was maintained at 37±1C.

The polarization cycle was initiated at -100 mv versus a saturated calomel electrode (SCE) by application of a potential of +100 mv to the counter electrode of the corrosion cell. Each specimen (working electrode) was polarized anodically at a rate of 10 mv per sec with the use of a programmable potentiostat.<sup>¶</sup> Polarization was allowed to proceed anodically until a three-decade increase in current density was experienced by the working electrode. Then the direction of change of the impressed potential was reversed. Completion of the polarization cycle was marked by return of the externally applied potential of a value of -100 versus SCE.

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# Olympia (noble metal content 90%), J. F. Jelenko and Co., Pennwalt Corp., New Rochelle, NY 10801.

§ Cutter Laboratories, Inc., Berkeley, CA 94710.

¶ Universal Programmer, Model 175, Analytical Instrument Division. Princeton Applied Research Corp., Princeton, NJ 08540.

Output of the potentiostat was monitored continuously on a Cartesian coordinate recorder.<sup>Ω</sup> Graphic displays of changing current density with impressed potential produced anodic and cathodic potentiodynamic polarization diagrams which reflected the electrochemical behavior of the test substances in the chloride medium.

A schematic of the response of a typical active-passive alloy to cyclic polarization is presented in Figure 2.

The anodic polarization curves defined the active, passive and transpassive ranges of the alloys. Additionally, these plots yielded coordinate values for primary passive potential ( $E_{pp}$ ) and critical current density ( $I_c$ ). Intersection of the anodic and cathodic curves delineated corrosion potential ( $E_{corr}$ ) and corrosion current density ( $I_{corr}$ ).

#### Results

The response of the conventional type III alloy to cyclic polarization is depicted in Figure 3. The anodic component of the corrosion behavior diagram exhibited a relatively long active linear range and an abrupt active-passive transition. Breakdown of passivity occurred in the vicinity of +800 mv versus SCE. Onset of the depression of anodic current density at an applied potential of 1,600 mv versus SCE was coincident with reversal of the direction of the scan. Behavior of the alloy became predominately cathodic at an impressed potential of approximately +900 mv versus SCE. The cathodic reduction curve

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<sup>Ω</sup> X-Y Recorder, Model 9002A, Analytical Instrument Division, Princeton Applied Research Corp., Princeton, NJ 08540.



intersected the passive region of the anodic polarization curve. Respective values for corrosion potential ( $E_{corr}$ ) and corrosion current density ( $I_{corr}$ ) were +530 mv versus SCE and  $4.1 \times 10^{-3}$  ma/cm<sup>2</sup>.

The behavior of the high-fusing crown-and-bridge alloy is illustrated in Figure 4. Current density required to elicit active-passive transition was one decade less than that required for the passivation of Oro B-2. The high-fusing alloy passivated weakly over a 700 mv range of impressed anodic potentials. Breakdown potential was approximately 900 mv anodic to the reference electrode. Reversal of the direction of change of the applied potential brought about an immediate decrease in anodic current density. Onset of the reduction phase of the cyclic response occurred at a relative noble potential of +655 mv versus SCE. The cathodic reduction curve intersected the passive region of the anodic polarization curve. Corrosion potential ( $E_{corr}$ ) and corrosion current density ( $I_{corr}$ ) were +600 mv versus SCE and  $0.94 \times 10^{-3}$  ma/cm<sup>2</sup>, respectively.

The responses of Neycast, Midas and Minigold to cyclic polarization were remarkably similar. A corrosion behavior diagram for one of these materials (Neycast) is shown in Figure 5. Critical current density required for passivation of the economy alloys was of the same order of magnitude as that required for passivation of Oro B-2. However, the range of potentials over which the low golds remained passive was relatively short. Breakdown of passivity occurred at potentials in the vicinity of +300 mv versus SCE. An immediate decline of the anodic current density of Neycast, Midas and Minigold accompanied scan reversal.

The cathodic reduction curves of the three economy alloys intersected the transpassive regions of their anodic polarization curves. Respective corrosion potentials ( $E_{\text{corr}}$ ) of Neycast, Midas and Minigold were +600, +650 and +540 mv versus SCE. Corrosion current densities of these materials were a decade higher than those of either Oro B-2 or Olympia.

#### Discussion

Understandably, caution must be exercised in the extrapolation of electrochemical data to clinical experience. Nonetheless, an appreciation of potential-current density relationships is essential to the rational application of crown-and-bridge alloys.

An alloy exposed to a corrosive will, in time, spontaneously reach its equilibrium (corrosion) potential. The degree of activity or passivity exhibited by an alloy at equilibrium with its environment is governed by compositional and structural features of the alloy and by the oxidizing power of the environment.

At a chloride ion concentration comparable to that of human saliva<sup>1</sup> (~24 m Eq/L), all materials considered in the present study exhibit active-passive transition. However, at their respective equilibrium potentials, Neycast, Midas and Minigold undergo active dissolution. Passivity at equilibrium is shown only by Oro B-2 and Olympia.

Corrosion behavior diagrams comparable to those of the economy alloys have been constructed for certain industrial and experimental alloys.<sup>2</sup> The corrosion resistance of chromium-platinum alloys to oxidizing acids is markedly inferior to the corrosion resistance of pure chromium. In hot concentrated nitric acid the corrosion potential

of chromium is very near the transpassive region. Alloying with, or coupling to a more noble substance produces a mixed potential within the transpassive region and a correspondingly high corrosion rate.

The electrochemical profiles of the economy alloys suggest that (1) the structures of Neycast, Midas and Minigold are biphasic; (2) the corrosion characteristics of the phases of each alloy are disparate; (3) the corrosion potential of the least noble phase lies within a relatively short range of passive potentials and (4) the more noble phase is unattacked by the test solvent. These factors would appear responsible for shifting of the equilibrium potentials of the low golds. to the transpassive regions of their anodic polarization curves.

It must be emphasized that the present findings on the economy alloys should not be construed as definitive demonstration of inadequate corrosion resistance. The findings have, however, prompted interest in the long term observation of restorations fabricated from these materials. Accordingly, an appropriate clinical study has been initiated.

#### Summary

The responses of five dental golds to in vitro cyclic potentiodynamic polarization were studied. The equilibrium behavior of two relatively noble alloys was characterized by passivity, whereas that of three materials of lesser nobility was typified by active dissolution. Clinical significance of the findings on the latter materials is uncertain and remains to be studied.

#### References

1. Shannon, I. L.: A Formula for Human Parotid Fluid Collected without Exogenous Stimulation. J Dent Res 46:309, 1967.
2. Greene, N. D.: Predicting Behavior of Corrosion Resistant Alloys by Potentiostatic Polarization Methods. Corrosion 18:136-142, 1962.

#### Legends for Figures

- Figure 1. Specimen holder for cyclic polarization test.
- Figure 2. Corrosion behavior diagram of a typical active-passive alloy.
- Figure 3. Corrosion behavior diagram for a conventional type III dental casting gold.
- Figure 4. Corrosion behavior diagram for a high-fusing crown-and-bridge alloy.
- Figure 5. Corrosion behavior diagram for an alloy of relatively low noble metal content.



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